RAW MATERIALS

UDC 666.123.22:661.3.004.14

SODA ASH BASED ON NEPHELINE MATERIAL USED IN THE GLASS INDUSTRY

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Translated from Steklo i Keramika, No. 7, pp. 13 – 16, July, 2003.

The physicochemical and technological properties of an improved modification of soda ash from nepheline material and its effect on batch preparation and silicate and glass formation and on the properties of glass are considered. It is established that the improved modification of soda with respect to its physicochemical and technologies properties and storage behavior belongs to the "heavyweight" category, is a promising alkali-bearing material, and can be recommended for effective application in the production of glass containers and household and sheet glass, including decorative float glass with special properties.

Soda is the most expensive material of all materials used in glass production [1 – 3]. Consequently, research oriented to the development of new kinds of alkaline materials or improving material properties is topical, since it compensates for the scarcity of raw materials and expands the list of materials available for the glass industry.

The main producer of soda ash from nepheline materials in Russia is the Russian Aluminum (RUSAL) Company, which carries out a full technological cycle since it owns a nepheline and a lime mine, and the Achinskii Alumina Works (AGK) processing mineral ore into alumina, potassium sulfate, potash, and soda ash. The RUSAL Company is carrying out a comprehensive upgrade of the AGK Works and has introduced some amendments to the technology of nepheline-based soda production to meet the standard requirements for alkaline materials used in the glass industry (GOST 5100–85) [3].

The present paper lists the results of integrated studies of the physicochemical and technological properties of an improved modification of soda ash based on nepheline materials developed by the RUSAL Company (hereafter "RUSAL soda," i.e., technical soda ash based on nepheline materials of improved modification, 2003).

The relative characteristics of alkaline-bearing materials are listed in Table 1.

The improved modification of soda differs from soda produced at the Achinskii Alumina Works (hereafter "AGK soda," i.e., technical soda ash based on nepheline material, GOST 10689–75, 1999) in its high and stable content of the main components, the presence of sodium chloride, and a significantly lower content of potassium carbonate and sulfur and iron compounds.

X-ray phase analysis of the mineralogical composition of soda produced by different manufacturers corroborate the presence of anhydrous sodium carbonate Na_2CO_3 as the main phase in the RUSAL soda (Fig. 1).

An important parameter is the granulometric composition of material [2, 3]. Sieve analysis indicated that the soda considered consists of single granules sized from 0.125 to 1.0 mm and does not contain dust-like particles. Granulometric laser microanalysis identified the presence of particles sized 0.125 – 0.300 mm up to 67% and 0.4 – 1.0 mm up to 25%.

Differential-thermal analysis of alkaline materials performed on a OD-103 derivatograph in polythermal conditions in the temperature interval of 20 – 1000°C with a heating rate of 10 K/min confirmed a low content of impurity components in the soda considered, whereas the absence of an endothermic effect within a temperature interval of 110 – 130°C is evidence of an insignificant content of crystallization and adsorption moisture.

The effect of the improved modification of soda on batch preparation and glass melting was studied based on an industrial batch for container glass and float glass using the polythermic method, thermogravimetric (DTA) analysis, and Zak – Ponomarev method to determine the melting rate

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0361-7610/03/0708-0208$25.00

TABLE 1

Properties of alkali-bearing materials	Soda produced by Soda JSC (Sterlitamak)		Technical soda ash from nepheline material	
	"lightweight"	"heavy" (granulated)	AGK	RUSAL, improved modification
Exterior appearance	White powder	White or grayish granules	Grayish-white powder	Small white granules
Chemical composition, %:				
Na_2CO_3	99.13	99.31	90.5	97.77
NaCl	0.42	0.52	–	0.12
K_2CO_3	–	–	5.0	1.10
K_2SO_4	–	–	4.4	0.46
Na_2SO_4	0.05	0.02	–	–
Fe_2O_3	0.003	0.002	0.01 – 0.02	0.001
Bulk density, g/cm^3	0.63	0.9 – 1.0	1.23	1.05
Melting point, °C	852	830	810	830

of experimental mixtures in laboratory and industrial conditions [4].

The technological suitability of a material primarily depends on its behavior in storage. Table 2 shows the data on the quality of RUSAL soda stored between February and June 2003.

It should be noted that after the content of the potassium component (K_2CO_3, K_2SO_4) in the new modification was corrected, this eliminated the most significant drawback of AGK soda previously registered in production, namely, its high hygroscopicity, which used to impaired the quality of soda in storage and had a negative effect on the quality of the batch [5, 6]. The improved soda modification does not cake or clot in storage, has high fluidity, and can be easily mixed with other batch components. Batch preparation cyclograms for the new variety of material were tested on existing machinery of the batch-preparation division.

It was established that replacement of alkaline material does not call for special techniques or modification of batch-preparation technologies and can be implemented without stopping a continuous process. The finished batch is classified as quality categories I and II.

The polythermic method makes it possible to monitor qualitative transformations occurring in a batch in heating and to identify the temperature bound of these transformations. The following batches were prepared for comparative studies: EB1) experimental batch based on lightweight soda produced by Soda JSC, Sterlitamak, EB2) experimental batch based on heavy soda produced by Soda JSC, Sterlitamak, EB3) experimental batch based on technical soda ash from nepheline material, grades 2 and 3 (GOST 10689–75) produced by the AGK company (1999); EB4) experimental batch based on the improved modification of technical soda ash from nepheline material produced by the RUSAL company (2003).

The diagrams obtained after a 2-h exposure of experimental batches in a temperature interval of 600 – 1400°C (Fig. 2) show that all batches have good melting properties,

TABLE 2

Storage time, months	Mass content in soda, %	
	Na_2CO_3	moisture
2	97.69	0.47
4	97.57	0.59
Initial soda	97.77	0.36

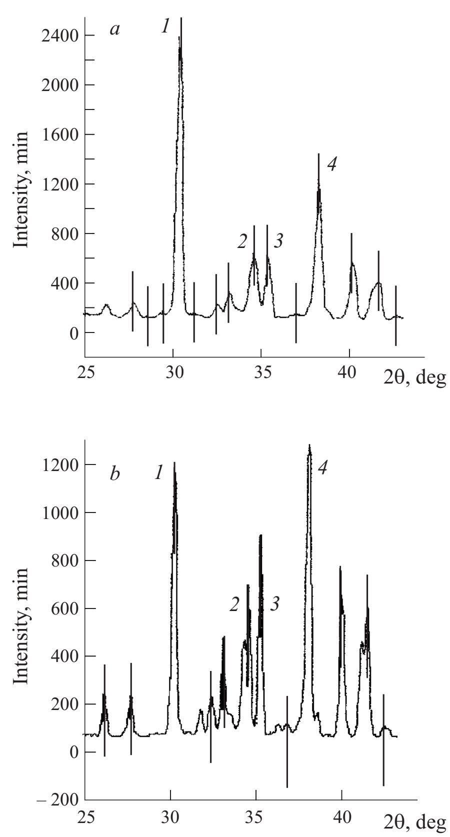

Fig. 1. Diffraction patterns of soda produced by Achinskii Alumina Works (AGK) (*a*) and by Soda JSC (*b*): *1*, *2*, *3*, and *4*) $d = 2.89$, 2.60, 2.54, and 2.36 Å, respectively.

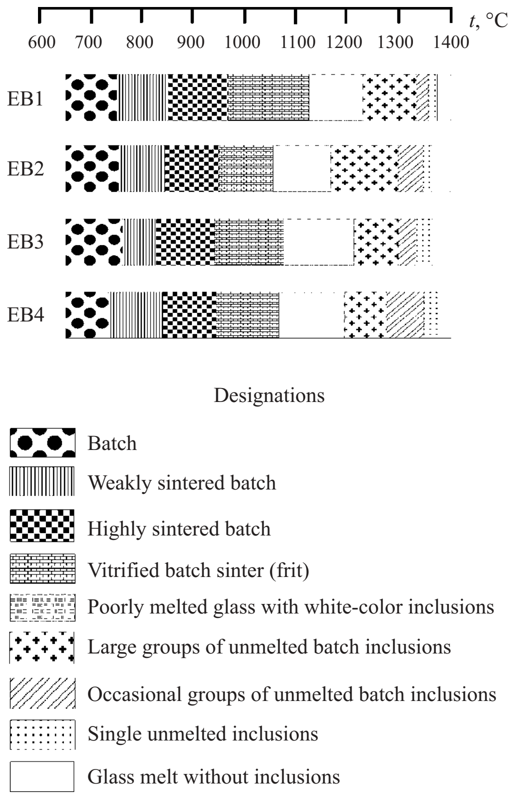

Fig. 2. Batch melting diagrams.

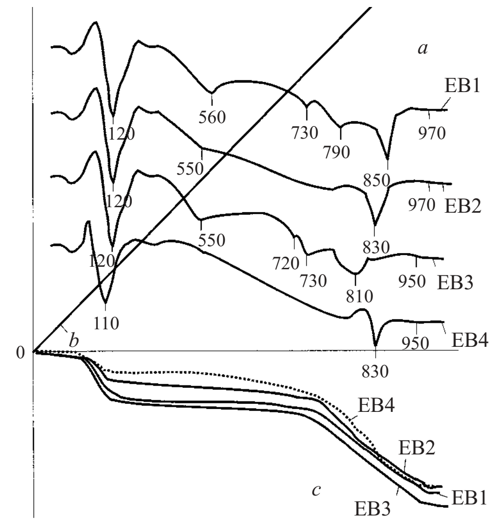

Fig. 3. Thermograms of experimental batches: *a*) thermal effect (DTA) curves of batches; *b*) heating curve; *c*) batch weight loss (TG).

but the processes of silicate and glass formation in the experimental batch based on RUSAL soda are shifted to a lower temperature range. The completely melted glass bounds in batches EB2 and EB4 are close, and the dissolution of residual quartz grains proceeds similarly. The results obtained are given below (the melting temperature is 1400°C).

Experimental batch	Glass formation duration, min
EB1	80
EB2	78
EB3	72
EB4	77

The shape of the DTA curves (Fig. 3) points as well to the similarity of the main processes in batches EB4 and EB2. Thus, moisture is removed from the batch components within a temperature interval of 20 – 250°C, which is shown by endothermic effects at 110 – 120°C. The processes of decomposition of batch components that are typical of glass melting proceed smoothly within a temperature range of 300 – 760°C. Sodium and potassium carbonates decompose starting at a temperature of 760°C, the maximum effect being registered at 830°C. The silicate formation process ends in batch EB4 at 950°C and in batch EB2 at 970°C. It is known that the maximum volatilization of gaseous components from a glass melt occurs at the stages of silicate and glass formation [7]. Thus, it follows from the TG curves that since the considered soda variety contains less impurity components, which decompose emitting gases, the total weight losses in batch EB4 is 20%, whereas the weight loss in batch EB3 is 24%, which is confirmed by the results of melting in a laboratory silit furnace at the maximum temperature of 1450°C. Thus, the height of melt foaming is significantly less in batch EB4 than in the other experimental batches.

The next stage of research was testing the RUSAL soda in experimental industrial production in a batch gas-flame furnace of capacity 600 kg, in which the batch and glass melt are heated by the thermal radiation energy of the flames and the furnace brickwork.

The main research-and-industrial production at the Saratov Institute of Glass is bulk-tinted light-and-heat-shielding glass of a wide color range [8]. This production is based on a directed control of the redox potential of the glass melt, in order for required color centers to be formed in glass melting, i.e., the absorption centers in the infrared and visible spectra ranges. Substitution of the main alkali component of the batch is an important technological factor since it can result in imperfect color and change the light transmission of glass in the infrared spectrum range, which in turn can cause cooling or overheating of the glass melt.

Light-and-heat-shielding glass TB-2 of bronze color was selected for comparative studies. The reference batch was a batch based on traditional lightweight soda produced by the Soda JSC. Experimental batches were prepared following one and the same cyclogram. The batch had category II and moisture 4.2%.

The time-temperature schedules were strictly observed in the synthesis of experimental glasses: the batch was loaded in five portions of 120 kg every 3 h, the rate of temperature rise to the maximum temperature was 50 K/h, and the maximum melting temperature was 1470°C.

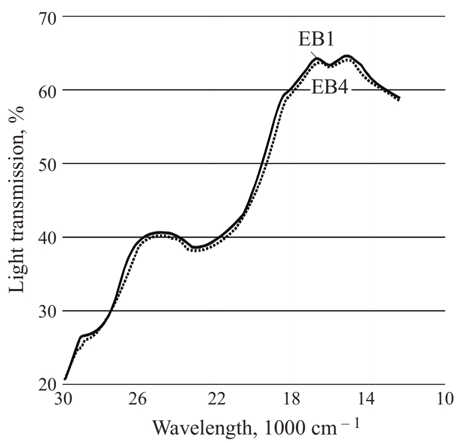

Fig. 4. Spectral transmission curves of glasses synthesized.

The criteria of the melting capacity of batches were easy casting and production of well melted and clarified glass.

The effect of the soda considered on melting and working properties was estimated by visual evaluation of the quality of melt samples taken every 2 h after reaching the maximum temperature inside the furnace and by the total time consumed in melting glass to complete clarification.

It was noted in the experiment that melting of experimental batch EB4 differs somewhat from the reference batch EB1. The batch portion loaded (having equal weight) was more compact. Fusion in the surface layer started 5 min after charging (in the reference batch 8 min after charging). Melting of both batches was accompanied by intense gas emission. The foam formed at the initial stage of melting EB4 was denser. The glass melt samples of both batches had up to 40 – 45% unmelted inclusions of size 0.2 – 0.8 mm. At the end of melting up to 1.2% unmelted grains sized 0.1 – 0.3 mm were observed in the reference batch samples, whereas in the experimental batch their content was less than 1%. Visual and microscope inspection of samples revealed that the last unmelted grains in the experimental batch disappeared after 16.5 h of melting, whereas in the reference batch they disappeared after 17.6 h. However, the total duration of melting and clarification of glass melt of batches EB1 and EB4 is equal and amounts to 23 h. The glass obtained has the following characteristics: clear, bronze color, light transmission (for thickness 5 mm) in the visible spectrum range (380 – 750 nm) 55.5% and in the IR range (750 – 2500 nm) 63.5%, which correlates with the parameters of glass TB-2 (TU-5922-210-05524989–02). The replacement of the alkaline material did not modify the shape of the spectral curves (Fig. 4). The glass synthesized has a saturated color tone and luster due to the presence of up to 1% K_2O in the alkali-containing material.

Thus, use of the improved soda modification did not require changes of the melting schedule, and industrial testing corroborated the conclusions of the laboratory studies.

Using the polythermic method and the mass crystallization method, it was found that experimental glass EB4 has a certain tendency for crystallization: its liquidus temperature (the upper crystallization bound) is 1015 – 1020°C and the emerging crystalline phase is β-wollastonite.

Main Properties of Container Glasses Synthesized in Laboratory Conditions Using New Alkaline Materials

Density, kg/m^3	2490
TCLE, 10^{-7} K^{-1}	88
Chemical resistance, hydrolytic class	3
Light transmission at wavelength 540 nm (d = 3 mm), %	87

Properties of Glasses EB4 Synthesized in Experimental-Industrial Conditions

Technological properties	
Temperature, °C:	
melting	1480 – 1500
working	1050 – 1100
Upper crystallization bound, °C	1015 – 1020
Chemical properties	
Weight loss, %, in treatment:	
in 0.01 N HCl	0.80
in 1 N NaOH	0.26
Physicochemical properties	
Density, kg/m^3	2504
TCLE, 10^{-7} K^{-1}	85.6
Service properties	
Heat resistance, number of cycles	At least 80
Water absorption, %	0

The studies performed established that the use of the new kind of alkaline material, namely, an improved modification of soda ash based on nepheline material:

– does not require modification of technology or more complicated equipment for batch preparation and glass melting;

– does not cause difficulties in batch formula calculation or in storage of material, including environmental-related aspects;

– transition to a new kind of alkaline materials can be implemented without stopping production and without lowering the quality of the product;

– analysis of the properties of glass synthesized did not reveal any deviations in its main technological parameters and physicochemical and service characteristics.

Consequently it can be stated that the improved modification of soda ash based on nepheline material produced by the RUSAL Company differs significantly from soda previously produced by the AGK Company (GOST 10684–75).

According to its physiochemical and technological properties and behavior in storage, soda produced by the RUSAL is a “heavy” variety, a promising alkali-bearing material, and can be recommended for effective application in the production of container glass and household and sheet glass, including decorative float glass with specialized properties.

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